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Phonons in some fluoride scheelites

P Nayak* and S Mohanty
P G Department of Physics, Sambalpur University, Jyoti Vihar, Sambalpur-768 019, Orissa, India
E-mail : mayakpb@hotmail.com

Abstract : The infrared and Raman scattering measurement on some Fluoride Scheelites have revealed two facts. These are (i) absence of several modes in the spectrum, which is thought to be either due to their non-identification or of non-observed nature and (ii) softening of few specific phonon modes in some systems. To account these unusual observations in some systems we propose a strong electron-phonon interaction in these systems. We consider the Periodic Anderson Model (PAM) with electron-phonon interaction as applied to Heavy Fermion (HF) systems However unlike the case of HF systems, we conjecture the coupling of phonon with *f*-electrons is stronger compared to that of hybridization. With this we reproduce a large number of phonon peaks even in the static case ($\omega = 0$) and softening.

Keywords Fluoride Scheelites, electron-phonon interaction, periodic Anderson model, spectral density function.

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1. Introduction

$LiReF_4$ are the series of iso-structural ternary fluoride compounds, which are formed as the mixed system of ReF_3–LiF, where Re belong to the group of element from Luropium ($z = 63$) to Lutetium ($z = 71$). These compounds crystallize in the $CaWU_4$ (scheelites) structure with two molecules per primitive cell [1,2] and are generally referred as fluoride scheelites. These systems have become the subject of interest in recent years mainly because these are optically transparent and have applications in Laser and other quantum electronic devices. LiYF is the most used flouride laser host crystal generally doped with trivalent Rare earth and more recently with Uranium [3,4].

On consideration with the structural aspect of both Oxo- and fluoride scheelites, it is expected that there will be distinct changes in charges, electronegativities and masses when, in the lattice of fluorides, Ca^{2+} is replaced by Re^{3+}, W^{6+} by Li^+ and O^{2-} by F^-. Moreover due to close packing of scheelites, all quantum electronic and magnetic properties of the materials get influenced by lattice dynamics. Therefore, knowledge of lattice dynamics of $LiReF_4$ will be useful in connection with their applications in laser optics.

It can be shown that there are thirty six phonon modes with $q = 0$, which are redistributed among the irreducible representation of C_{4th} as

$$\Gamma^{vib} = 3Ag + 5Bg + 5Eg + 5Au + 3Bu + 5Eu.$$

Out of these all *u* modes are infrared active except one Au and an Eu mode and all *g* modes are Raman active. However, some experiments [1,4] concerning Raman scattering and infrared spectroscopy in some flouride scheelite systems have reported two important facts. These are (i) frequencies of several modes are thought to be missing, which are neither identified nor observed and (ii) softening of some phonon modes. To overcome those deficiencies and for a confirmation of earlier results, Salaun *et al*, [5,6] conducted infrared measurements on some of $LiYF_4$ and $LiLnF_4$ compounds with Ln = Ho, Er, Tm and Yb and Raman spectra for Ln = Tm, Hb and Yb. Using group theoretical analyses they were able to give data related to effective changes, the frequency dependence of the optical parameters and atomic movements under some of the vibrational mode. Moreover, they were able to explain low-lying Ag modes not predicted earlier. In addition, their measurements at different temperatures show clear evidence of phonon softening in

*Corresponding Author

specific modes of certain systems. Their measurements from room temperature to 40° K revealed the fact that the line widths decrease and the frequencies slightly increase except for few specific Bg, Eg symmetric modes of the $LiTmF_4$ compound. The decrease of these few specific modes, which is unusual, is attributed to electron-phonon coupling.

To account for the phonon softening and missing phonon lines in the Raman spectra we have proposed a strong electron-phonon coupling in these systems. In order to explain this we have considered the Heavy Fermion model of Nayak *et al*, [7,8], where the electron-phonon interaction is incorporated in the Periodic Anderson Model (PAM) without the Coulomb repulsion term. Fluoride scheelites being insulators the *f*-electron plays an important role. So, to calculate with our model for this system we have assumed that the interaction of *f*-electrons with phonons are stronger than that of phonons either with conduction electrons or with electrons in hybridized bands. In order to compare our result with experiments it is necessary to know the phonon spectral density function. Double time Green's function technique [9] is used to calculate this function.

We calculate the phonon response function to see how the phonon gets modified through the response functions of the conduction electrons, *f*-electrons and *f-d* mixing densities. The spectral density function is calculated. It involves various model parameters namely, the position of *f*-level, the effective coupling strength and the electron-phonon coupling strength. Keeping the former two parameters fixed, the softening behavior of phonons with temperature for different strength of electron-phonon coupling is studied. It is observed that even in the static limit the present work provides large number of phonon peaks of various strengths. There might be some missed phonon lines, which fact may be interpreted as, due to strong electron-phonon interaction the intensity is sufficiently lowered so as not to be observed in the experiment.

2. Formalism

We consider the model system with the Hamiltonian

$$H = H_0 + H_{e-p} + H_p \tag{1}$$

which consists of three terms (i) the electronic Hamiltonian H_0, (ii) the electron-phonon interaction term H_{e-p} and (iii) the Hamiltonian for the phonons H_p. The explicit forms of these are given by

$$H_0 = \sum_{k\sigma} \varepsilon_k C^\dagger_{k\sigma} C_{k\sigma} + E_0 \sum f^\dagger_{k\sigma} f_{k\sigma} + \gamma_0 \sum_{k\sigma} \left(f^\dagger_{k\sigma} C_{k\sigma} + C^\dagger_{k\sigma} f_{k\sigma} \right), \tag{2a}$$

$$H_{e-p} = \sum_{kq\sigma} \left[f_1(q) \left(f^\dagger_{k+q,\sigma} C_{k,\sigma} + C^\dagger_{k+q,\sigma} f_{k,\sigma} \right) + f_2(q) f^\dagger_{k+q,\sigma} f_{k,\sigma} \right] \left[b_q + b^\dagger_{-q} \right], \tag{2b}$$

$$H_p = \sum \omega_q b^\dagger_q b_q, \tag{2c}$$

where $C^\dagger_{k\sigma}(C_{k\sigma})$ and $f^\dagger_{k\sigma}(f_{k\sigma})$ are the creation and annihilation operators for conduction and *f*-electrons with momentum k and spin s respectively. $\hat{\varepsilon}_k$ is the energy of an electron in the conduction band, E_0 is the position of *f*-level, $n^f_{i\sigma} = f_{i\sigma} f^\dagger_{i\sigma}$ is the number operator for *f*-electron, and g_0 represents the strength of the hybridization between the *f*-electrons and the conduction electrons. Here, $f_1(q)$ and $f_2(q)$ are the coupling constants, the former corresponding to the interaction arising between phonons with the electrons of the hybridization band and the later corresponding to the strength of interaction with *f*-electrons. $b^\dagger_q(b_q)$ is the creation (annihilation) operator for the phonons with the wave vector q and frequency w_q.

Since we are interested in the calculation of the phonon response functions, *i.e.* the spectral density functions it is required to evaluate the phonon Green function defined as

$$D_{qq'}(t-t') = \left\langle\left\langle A_q(t); A_{q'}(t') \right\rangle\right\rangle = -i\theta(t-t') \left\langle \left[A_q(t); A_{q'}(t') \right]_- \right\rangle, \tag{3}$$

where $A_q = b_q + b^\dagger_{-q}$ and $B_q = b_q - b^\dagger_{-q}$ (4)

are respectively the q-th Fourier component of the displacement and momentum of the ions.

The Fourier transformed Green function $D_{qq'}(\omega)$ can be calculated by writing its equation of motion using the Hamiltonian of eq. (1), which can be expressed in the form :

$$D_{qq'}(\omega) = \delta_{-qq'} (\omega_q/\pi) \left[\omega^2 - \omega_q^2 - 4\pi\omega_q \chi_{qq}(\omega) \right]^{-1}, \tag{5}$$

where the Fourier transform of the response functions entering in the self-energy is given by

$$\chi_{qq'}(\omega) = \sum_{kk'\sigma\sigma'} \left[f_1(-q) f_1(-q') \Gamma_1(kq, k'q', \sigma) + f_1(-q) f_2(-q') \Gamma_2(kq, k'q', \sigma) + f_2(-q) f_1(-q') \Gamma_3(kq, k'q', \sigma) + f_2(-q) f_2(-q') \Gamma_4(kq, k'q', \sigma) \right]. \tag{6}$$

Here, G_i's (i = 1 to 4) represent the electron response functions. These electron response functions are higher orde

Green functions of the electron operators and have a strong influence on the phonon spectrum and spectral density function. These are evaluated through equations of motion using the electronic part of the Hamiltonian without the phonon and the electron-phonon term.

The phonon excitation spectrum depends on different model parameters through the electron response functions, which in turn affect in the spectral density function, that is defined through the equation :

$$S(q,\omega) = -2\,\mathrm{Im}\,D_{qq'}(\omega + i\eta). \tag{7}$$

Replacing $\sum_k = \int d\varepsilon_k N(\varepsilon_k)$, the final form of χ can be obtained as

$$\chi_{qq'}(\omega) = \{f_1^2(q)N(\varepsilon_F)/\pi\} \times \int [\Gamma_1(k,q,\omega) + \{f_2(q)/f_1(q)\} \times \{\Gamma_2(k,q,\omega) + \Gamma_3(k,q,\omega)\} + \{f_2(q)/f_1(q)\}^2 \Gamma_4(k,q,\omega)] d\varepsilon_k. \tag{8}$$

Substituting this into eq. (5) and evaluating the real and imaginary parts of $D_{qq'}(\omega + i\eta)$ by substituting $\omega \to \omega + i\eta$, the correct form of the spectral density function is expressed as

$$S(q,\omega) = \frac{2}{\pi\omega_q}\{(\eta/\omega_q^2) - (4\pi/\omega_q)\,\mathrm{Im}\,\chi_{qq}\} \times \left[\{(\omega/\omega_q)^2 - 1 - (4\pi/\omega_q)\,\mathrm{Re}\,\chi_{qq}\}^2 + \{(\eta/\omega_q^2) - (4\pi/\omega_q)\,\mathrm{Im}\,\chi_{qq}\}^2\right]^{-1}. \tag{9}$$

This equation is the final equation, which is to be evaluated numerically. It is exact and valid for all wave vector q and temperature T. The solution of this equation for finite q and T are quite complicated. Therefore, to avoid this, the numerical calculations are performed for $q = 0$ *i.e.* in the long wavelength limit for small temperature in the static limit *i.e.* $\omega = 0$.

We finally evaluate the spectral density function with these approximations, which is expressed as

$$S(q=0,\omega) = \frac{2}{\pi\omega_0}\{(\eta/\omega_0^2) - (4\pi/\omega_0)\,\mathrm{Im}\,\chi(q=0,\omega)\} \times \left[\{(\omega/\omega_0)^2 - 1 - (4\pi/\omega_0)\,\mathrm{Re}\,\chi(q=0,\omega)\}^2 + \{(\eta/\omega_0^2) - (4\pi/\omega_0)\,\mathrm{Im}\,\chi(q=0,\omega)\}^2\right]^{-1}. \tag{10}$$

3. Results and discussion

The dimensionless parameters which are involved in these calculations are the ratio of the two electron-phonon interaction strengths $r = f_2(0)/f_1(0)$ the coupling constant $g = N(0)f_1^2(0)/\omega_0$, $N(0)$ being the density of states at the Fermi level. The other parameters are the strength of hybridization γ_0, the position of the f-level $d = E_0/\gamma_0$, the bandwidth $W' = W/\gamma_0$ and the inverse of the temperature $b = \gamma_0/2KT$. These parameters play a dominant role on the phonon spectrum. Similarly the variable band energies are denoted by $y = \varepsilon_k/\gamma_0$, width of the phonon mode as $e = \eta/\gamma_0^2$ and the renormalized phonon frequency $c = \omega/\gamma_0$ is expressed as the product of reduced frequency $\tilde{\omega}(= \omega/\omega_0)$, and the scaling parameter $z = \omega_0/\gamma_0$, ω_0 being the frequency of the bare phonon.

For convenience, the Fermi level is set equal to zero and the value of d is kept negative, as these are rare-earth compounds, whose f-level lies deep to the core. The value of r is always kept more than one, so as to make $f_2(q)$ stronger than $f_1(q)$. The properties of phonon can be studied with these different parameters. However, due to lack of space we present only two of the important plots with two different values of d at different temperatures keeping other parameters g(= 0.01), r(= 2.0), z(= 0.01) and y(= 4.0) constant.

Figure 1 is the plot of spectral density function $S(q, 0)$ *versus* $\tilde{\omega}$ for $d = -3.0$, which show large number of peaks within the range between $\tilde{\omega} = 0.62$ to $\tilde{\omega} = 1.20$ for different temperatures *i.e.*, $b = 0.05$, 0.15 and 0.25. From temperature

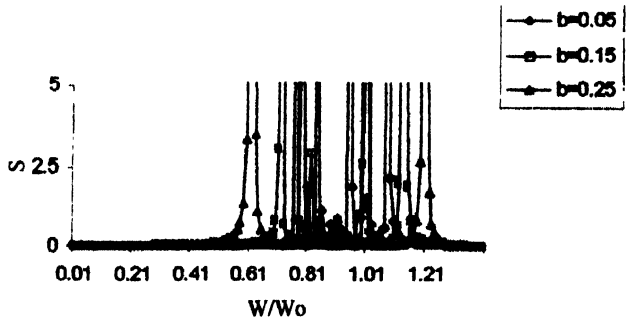

Figure 1. Plot of $\tilde{\omega}(= \omega/\omega_0)$ *versus* $S(q, 0)$ for $r = 2.0$, $g = 0.01$, $z = 0.01$, $y = 4.0$ and $d = -3.0$ for different temperatures $b = 0.05$, 0.15, 0.25.

variation at this value of d, some peaks are identified as phonon peaks as they shift and change in width. The other peaks are of electronic in nature, which remain constant through out the variation of temperature. Out of these about four and five peaks appeared at $\tilde{\omega} < 1$ and about three peaks appeared at $\tilde{\omega} > 1$. On comparing our result with that of Salaun *et al* [5], it has been found that there are

about eight phonon modes out of which four lies below and four above the value of ω_{TO}, which agrees with our findings.

Figure 2 is a similar plot for a different d value *i.e.*, $d = -2.0$. It is interesting to point out that number of phonon modes appearing above ω_{TO} have now reduced to one.

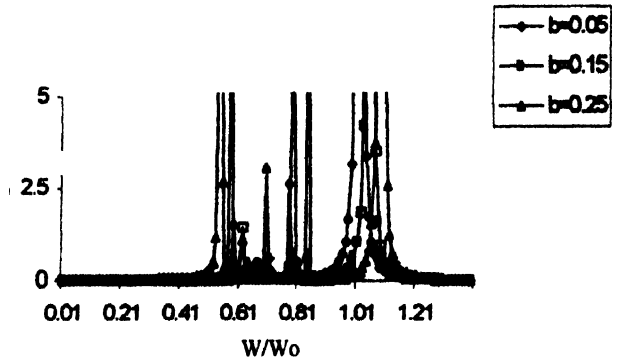

Figure 2. Plot of $\tilde{\omega}(=\omega/\omega_0)$ *versus* $S(q, 0)$ for $r = 2.0$, g 0.01, $z = 0.01$, $y = 4.0$ and $d = -2.0$ for different temperatures b 0.05, 0.15, 0.25.

This implies that for this value of d, some modes above ω_{TO} are either suppressed or have disappeared. This means, depending on the position of f-level and the strength of electron-phonon interaction, the magnitude of some of the phonon peaks are strongly reduced, as appears in the experiment. Moreover, these phonon modes shift as the temperature is varied. On comparing our results with experimental findings, it is concluded that our results show the existence of a large number of phonon peaks even in the static limit and softening which is in agreement with experimental results.

4. Conclusion

Here, an attempt has been made to explain the existence of strong electron-phonon interaction in some fluoride scheelites. To understand this mechanism microscopically, phonons are assumed to interact strongly with f-electrons compared to electrons of hybridization band. The spectral density function is calculated using Zubarev type Green function. To achieve this, the numerical analysis is performed for $q = 0$ in the static limit. The results so obtained give a qualitative agreement with experimental findings.

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